Multiple Oxidative Addition of $Ph_2(C_5H_4N)PSe$ to $[Ru_3(CO)_{12}]$ − Structural Characterization of $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ Containing Two Differently Metalated 2-Pyridyl Fragments

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The ligand $Ph_2(2\text{-}C_5H_4N)PSe$ undergoes multiple fragmentation by reaction with $[Ru_3(CO)_{12}]$ affording the 54-electron trinuclear complex $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)_2(\mu\text{-}C_5H_4N)(\mu_3\text{-}C_5H_4N)(CO)_6]$ (**1**) which does not contain any Ru–Ru bond and is built up by a unique synergism of five bridging ligands. Complex **1** contains two bridging pyridyl groups: the first one connects two ruthenium atoms through σ bonds and lies on the plane defined by the three metals; the second one is also σ-bound to two ruthenium atoms, and is nearly perpendicular to the metal plane in such a way that it appears to be involved in a weak π interaction with the third metal.

Introduction

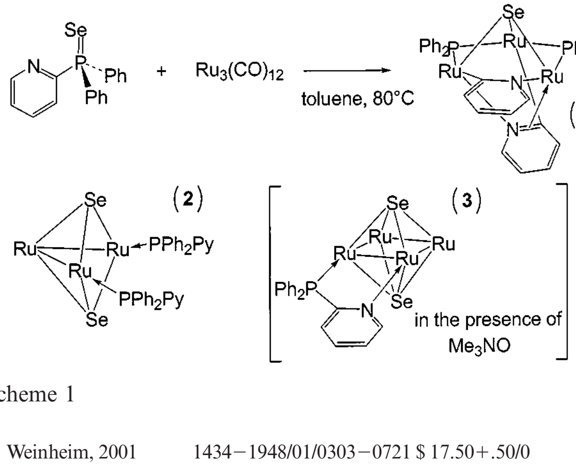
The chemistry of chalcogenido-carbonyl metal compounds comprises a variety of molecular architectures spanning from dinuclear metal species to giant molecular clusters.[1,2] In this context, systematic investigations carried out by our group on the reactivity of tertiary phosphane and diphosphane selenides, such as Ph_3PSe and $(Ph_2PSe)_2CH_2$ ($dppmSe_2$) towards $[M_3(CO)_{12}]$ (M = Fe or Ru) have shown that these reactions provide simple, sometimes selective synthetic routes to phosphane-substituted, selenido-carbonyl clusters.[3−5] Moreover, these processes lead in some instances to the formation of species not easily achievable by other paths, such as $[Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(dppm)]$, which is the first reported 72-electrons Ru−Se cubane-like cage complex.[6]

As a natural extension of these studies, we have considered the reactions of group-8 carbonyl clusters with tertiary phosphane selenides bearing heterocyclic moieties, such as the 2-pyridyl and 2-thienyl rings. The presence of these groups was expected to lead to new reactivity patterns in cluster growing processes, owing to the coordinating ability of the heteroatoms and to the possible release of heterocyclic fragments. In fact, we have recently found that the reaction of $Ph_2(C_4H_3S)PSe$ with $[Ru_3(CO)_{12}]$ affords the open triangular 50-electron cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(C_4H_3S)Ph_2\}_2]$ and the 48-electron cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(\mu\text{-}C_4H_3S)(CO)_6\{P(C_4H_3S)Ph_2\}]$ derived from the multiple fragmentation of one phosphane ligand on the metal triangle.[7]

Regarding the pyridyl derivative $Ph_2(2\text{-}C_5H_4N)PSe$, its parent compound $Ph_2(2\text{-}C_5H_4N)P$ (and related ligands) has been extensively used to bridge metal centres in dinuclear and cluster species.[8−10] However, faced with $[Ru_3(CO)_{12}]$ it undergoes a P−C cleavage expelling a phenyl ring,[11] the P−C(Py) bond remaining intact. On the other hand, pyridyl fragments on ruthenium and osmium clusters have been obtained by direct reactions with pyridine and related molecules.[12−15] The organometallic chemistry of nitrogen and sulfur heterocycles is further motivated by its relevance to the hydrodenitrogenation and hydrodesulfurization processes.[16]

Results and Discussion

The reaction between $Ph_2(2\text{-}C_5H_4N)PSe$ and $[Ru_3(CO)_{12}]$ affords the products shown in Scheme 1 (carbonyls omitted), whose distribution depends on the reaction conditions. Cluster **2** [*nido* core, seven skeletal electron pairs (sep)] should be regarded as the primary product of the oxidative attack of two selenide molecules to the metal triangle, whereas cluster **3** (*closo*, 7 sep) should derive from **2** through thermal condensation and ligand exchange processes. Clusters of these two families are generally the main



Scheme 1

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products in the reactions of iron and ruthenium carbonyls with phosphane selenides.[3]

In addition, the starting triruthenium triangle undergoes multiple oxidative attack by two P−C(Py) groups, resulting in the formation of the unprecedented compound [Ru_3(μ_3-Se)(μ-PPh_2)$_2$(μ-C_5H_4N)(μ_3-C_5H_4N)$(CO)_6$] (**1**), whose molecular structure is shown in Figure 1.

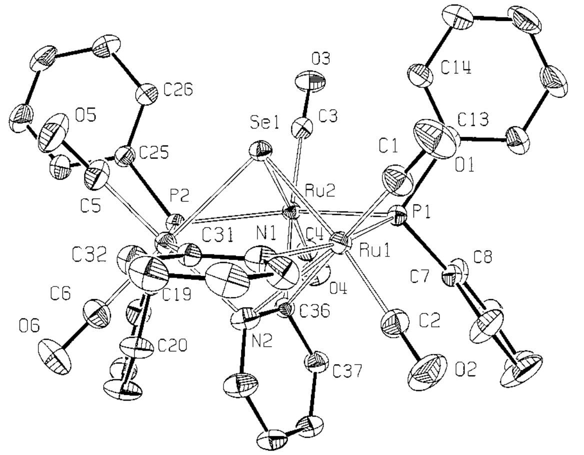

Figure 1. ORTEP diagram (30% probability level) of the molecular structure of **1** showing the atom numbering scheme; selected interatomic distances (Å): Ru(1)−Se(1) 2.515(1), Ru(1)−P(1) 2.433(1), Ru(1)−N(1) 2.173(2), Ru(1)−N(2) 2.619(3), Ru(1)−C(36) 2.822(3), Ru(2)−Se(1) 2.599(1), Ru(2)−P(1) 2.395(1), Ru(2)−P(2) 2.404(1), Ru(2)−C(36) 2.147(2), Ru(3)−Se(1) 2.550(1), Ru(3)−P(2) 2.416(1), Ru(3)−N(2) 2.171(2) Ru(3)−C(31) 2.128(2), N(1)−C(31) 1.348(3), N(2)−C(36) 1.353(3), Ru(1)···Ru(2) 3.351(1), Ru(1)···Ru(3) 3.442(1), Ru(2)···Ru(3) 3.476(1)

The structure of this polynuclear species is characterized by the presence of a nearly planar array of eleven atoms forming two roughly coplanar fused rings, i.e. the heptaatomic RuPRuPRuCN cycle and one pyridyl ring [dihedral angle 6.9(1)°]. The selenido ligand bridges three noninteracting ruthenium(II) atoms, and is elevated over the mean plane defined by the heptaatomic ring by 1.62 Å. This value is significantly lower than the mean distance of the selenium atoms from the Ru_4 plane (1.82 Å) observed in the Ru_4Se_2 octahedral clusters,[3] as a consequence of the rather large Ru···Ru spans (average 3.42 Å). This μ_3-Se bridging mode, connecting three noninteracting metal atoms, has two precedents in another trinuclear ruthenium compound containing a phosphazene ligand[17] and in a triosmium derivative.[18]

Another peculiarity of the structure of **1** is the presence of two different bridging fashions of the 2-pyridyl group. The first one [μ_2-η^1:η^1, concerning the N(1) ring] differs from those usually observed in the triangular Ru or Os clusters containing *N*-heterocyclic fragments, as these ligands currently occupy edge-bridging diaxial sites;[14] the present mode (coplanarity with the Ru_3 ensemble) is rather rare, being paralleled only by that observed in the bridged butterfly cluster [$HRu_5C(CO)_{14}(C_5H_4N)$].[19] The second bridging mode is adopted by the N(2) ring capping the trimetallic plane opposite to the selenium atom. N(2) and C(36) are σ-bound to Ru(3) and Ru(2), respectively, in such a way that the pyridine ring is nearly perpendicular to the plane defined by the three metal atoms (74°), and seems involved in a weak π interaction with the third metal. Although this interaction with Ru(1) appears quite weak [Ru(1)−N(2) 2.619(3), Ru(1)−C(36) 2.822(3) Å], it could be required to complete the coordination sphere of Ru(1) and is suggested by the orientation of the pyridine ring. In fact, the pyridine plane is inclined towards Ru(1) with respect to the Ru(2)−Ru(3) axis by 11.0°. Moreover, if we consider that the capping pyridyl group donates two π electrons to Ru(1), the whole set of ligands contributes 30 electrons to the structure, attaining the expected count of 54 electrons. This would be an unprecedented type of bridging mode for the pyridyl group, although it has been observed with the piperidyl ligand.[20] There is one other structure where the pyridyl fragment adopts a μ_3-bridging mode, but in a η^1:η^1:η^1 fashion.[21]

As a final remark, it should be emphasized that complex **1** is built up by a unique structural synergism of five bridging ligands. It has been obtained from Ph_2(2-C_5H_4N)PSe through P=Se and P−C(Py) bond cleavages, the latter process contrasting with the reactivity of Ph_2(2-C_5H_4N)P towards [$Ru_3(CO)_{12}$], which undergoes P−C(Ph) rupture,[11] as mentioned in the introduction. The different behaviour observed in this work could be due to the presence of capping selenido ligands, as observed in the case of diphenylthienylphosphane selenide.[7]

Experimental Section

General Remarks: The starting reagents [$Ru_3(CO)_{12}$], KNCSe, Ph_2(2-C_5H_4N)P and Me_3NO are pure commercial products (Aldrich and Fluka) and were used as received. The solvents (C. Erba) were dried and distilled by standard techniques before use. All manipulations (prior to the TLC separations) were carried out under dry nitrogen by means of standard Schlenk techniques. Elemental (C, H, N) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr discs or CH_2Cl_2 solutions) were recorded on a Nicolet 5PC FT spectrometer. ^1H (300 MHz), ^{31}P (81.0 MHz, 85% H_3PO_4 as external reference) NMR spectra ($CDCl_3$ solutions) were recorded on Bruker instruments, AC 300 (^1H) and CXP 200 (^{31}P).

Synthesis of Ph_2(2-C_5H_4N)PSe: A large excess of KNCSe (1.50 g, 10.4 mmol) was added to an acetonitrile (150 mL) solution of diphenyl-2-pyridylphosphane (0.70 g, 2.7 mmol); the solution was stirred at room temperature for 3 h, then the solvent was removed in vacuo and the residue was washed with water. The rough powder was recrystallized from ethanol, obtaining a white microcrystalline product (yield 85%). $C_{17}H_{14}PNSe$ (342.24): calcd. C 56.7, H 4.1, N 4.1; found C 57.2, H 3.9, N 4.0. − FTIR (KBr): $\tilde{\nu}$ = 569 cm^{-1} (PSe). − ^{31}P NMR ($CDCl_3$): δ = 31.5 [s, ^1J(P,Se) = 720 Hz]. − ^1H NMR ($CDCl_3$): δ = 8.71 [d, ^3J(H,H) = 4 Hz, 1 H, 6-Py], 8.61 [t, ^3J(H,H) = ^3J(H,P) = 6 Hz, 1 H, 3-Py], 7.92−7.34 (mm, 12 H, 2Ph, Py).

Reactions of $Ph_2(C_5H_4N)PSe$ with [$Ru_3(CO)_{12}$]: [$Ru_3(CO)_{12}$] (150 mg, 0.235 mmol) was reacted 1:2 with $Ph_2(C_5H_4N)PSe$ (161 mg, 0.469 mmol) in toluene at 70 °C for 1 h until the solution turned deep reddish brown. The mixture was evaporated to dryness and the residue was redissolved in a small amount of dichloromethane. TLC separation on silica, with a 1:1 dichloromethane/hexane as eluent mixture, yielded three products: a red band, a light orange one and a reddish orange one, in order of elution. Two trace products and some decomposition were also observed. The first product was identified as **1** after the solution of its crystal structure (yield 12%). The third reddish orange derivative was identified as $[Ru_3Se_2(CO)_7\{P\text{-}P(C_5H_4N)Ph_2\}_2]$ (**2**) by comparison of its ^{31}P NMR and FT-IR spectra with those of the related cluster $[Ru_3Se_2(CO)_7(PPh_3)_2]$[22] (yield 32%). The identity of the second product is under investigation. Compound **1**: FTIR (CH_2Cl_2): $\tilde{\nu}$ = 2021 s (CO), 2013 sh, 1964 s cm^{-1}. – $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 49.0 (d), −18.6 [d, ^2J(P,P) = 166 Hz]. – ^1H NMR ($CDCl_3$, 25 °C): δ = 8.52 [d, ^3J(H,H) = 6 Hz, 1 H Py], 7.91−6.62 (m, 13 H, 2Ph, Py).

The same 1:2 reaction was carried in the presence of Me_3NO (18 mg, 0.24 mmol) and gave a deep red solution; it was processed as in the previous case, yielding, in order of elution, **1** (10%), $[Ru_4Se_2(CO)_9(\mu\text{-}P,N\text{-}Ph_2(C_5H_4N)P)]$ (**3**) (light orange 22%) and **2** (7%), along with an unidentified species and some decomposition. Cluster **3** was identified by comparison of its IR spectral data with those of the analogous dppm derivative.[4] Purification by crystallization (from a CH_2Cl_2/MeOH mixture at 5 °C for some days) gave well-formed crystals of **1** suitable for X-ray analysis.

X-ray Structural Analysis: Cluster **1**, $C_{40}H_{28}N_2O_6P_2Ru_3Se$, M = 1076.75 triclinic, space group $P\bar{1}$, a = 16.619(4) Å, b = 12.494(3) Å, c = 10.214(5) Å, α = 98.49(4)°, β = 111.28(6)°, γ = 106.70(2)°, V = 2000(1) Å^3, Z = 2, D_c = 1.788 g·cm^{-3}, $F(000)$ = 1052, graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, μ = 21.56 cm^{-1}. Philips PW 1100 diffractometer, $\theta-2\theta$ scan technique at room temperature. 11672 Unique reflections measured (with θ in the range 3−30°) and used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2), using the SHELX-97 system of crystallographic computer programs.[23] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed at their geometrically calculated positions and refined riding on their parent atoms; final wR_2 = 0.0688 and R_1 [for 8871 reflections with $I > 2\sigma(I)$] 0.0272; weighting scheme used in the last cycles of refinement $w = 1/[\sigma^2F_o^2 + (0.0365\,P)^2]$, where $P = (F_o^2+2F_c^2)/3$. Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147775. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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